

# Molecular Magnetism

## The Electronic Hamiltonian

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# Hamiltonian mechanics

- ▶ In classical **Hamiltonian mechanics**, a system of particles is described in terms their **positions**  $q_i$  and **conjugate momenta**  $p_i$ .
- ▶ For each such system, there exists a scalar **Hamiltonian function**  $H(q_i, p_i)$  such that the classical equations of motion are given by:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (\text{Hamilton's equations of motion})$$

- ▶ Example: a single particle of mass  $m$  in a conservative force field  $F(q)$ 
  - ▶ the Hamiltonian function is constructed from the corresponding scalar potential:

$$H(q, p) = \frac{p^2}{2m} + V(q), \quad F(q) = -\frac{\partial V(q)}{\partial q}$$

- ▶ Hamilton's equations are equivalent to Newton's equations:

$$\left. \begin{aligned} \dot{q} &= \frac{\partial H(q, p)}{\partial p} = \frac{p}{m} \\ \dot{p} &= -\frac{\partial H(q, p)}{\partial q} = -\frac{\partial V(q)}{\partial q} \end{aligned} \right\} \Rightarrow m\ddot{q} = F(q) \quad (\text{Newton's equations of motion})$$

- ▶ Note:
  - ▶ Newton's equations are second-order differential equations
  - ▶ Hamilton's equations are first-order differential equations
  - ▶ the Hamiltonian function is not unique!

# Quantization of a particle in conservative force field

- ▶ The Hamiltonian formulation is **more general** than the Newtonian formulation:
  - ▶ it is invariant to coordinate transformations
  - ▶ it provides a uniform description of matter and field
  - ▶ it constitutes the springboard to quantum mechanics
- ▶ The Hamiltonian function (the total energy) of a particle in a **conservative force field**:

$$H(q, p) = \frac{p^2}{2m} + V(q)$$

- ▶ Standard rule for **quantization** (in Cartesian coordinates):
  - ▶ carry out the substitutions

$$\mathbf{p} \rightarrow -i\hbar\nabla, \quad H \rightarrow i\hbar\frac{\partial}{\partial t}$$

- ▶ multiply the resulting expression by the wave function  $\Psi(q)$  from the right:

$$i\hbar\frac{\partial\Psi(q)}{\partial t} = \left[ -\frac{\hbar^2}{2m}\nabla^2 + V(q) \right] \Psi(q)$$

- ▶ This approach is sufficient for a treatment of electrons in an **electrostatic field**
  - ▶ it is **insufficient for nonconservative systems**
  - ▶ it is therefore inappropriate for systems in a general electromagnetic field

# The Lorentz force and Maxwell's equations

- ▶ In the presence of an **electric field**  $\mathbf{E}$  and a **magnetic field** (magnetic induction)  $\mathbf{B}$ , a classical particle of charge  $z$  experiences the **Lorentz force**:

$$\mathbf{F} = z(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

- ▶ since this force depends on the velocity  $\mathbf{v}$  of the particle, it is not conservative
- ▶ The electric and magnetic fields  $\mathbf{E}$  and  $\mathbf{B}$  satisfy **Maxwell's equations** (1861–1868):

$$\nabla \cdot \mathbf{E} = \rho/\epsilon_0 \quad \leftarrow \text{Coulomb's law}$$

$$\nabla \times \mathbf{B} - \epsilon_0\mu_0 \partial\mathbf{E}/\partial t = \mu_0\mathbf{J} \quad \leftarrow \text{Ampère's law with Maxwell's correction}$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} + \partial\mathbf{B}/\partial t = \mathbf{0} \quad \leftarrow \text{Faraday's law of induction}$$

- ▶ Note:

- ▶ when the charge and current densities  $\rho(\mathbf{r}, t)$  and  $\mathbf{J}(\mathbf{r}, t)$  are known, Maxwell's equations can be solved for  $\mathbf{E}(\mathbf{r}, t)$  and  $\mathbf{B}(\mathbf{r}, t)$
- ▶ on the other hand, since the charges (particles) are driven by the Lorentz force,  $\rho(\mathbf{r}, t)$  and  $\mathbf{J}(\mathbf{r}, t)$  are functions of  $\mathbf{E}(\mathbf{r}, t)$  and  $\mathbf{B}(\mathbf{r}, t)$
- ▶ We shall consider the **motion of particles in a given (fixed) electromagnetic field**.

- ▶ The second, **homogeneous pair of Maxwell's equations** involves only **E** and **B**:

$$\nabla \cdot \mathbf{B} = 0 \quad (1)$$

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \quad (2)$$

- Eq. (1) is satisfied by introducing the vector potential **A**:

$$\nabla \cdot \mathbf{B} = 0 \Rightarrow \mathbf{B} = \nabla \times \mathbf{A} \quad \leftarrow \text{vector potential} \quad (3)$$

- inserting Eq. (3) in Eq. (2) and introducing a scalar potential  $\phi$ , we obtain

$$\nabla \times \left( \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0 \Rightarrow \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\nabla \phi \quad \leftarrow \text{scalar potential}$$

- ▶ The second pair of Maxwell's equations is thus automatically satisfied by writing

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

- ▶ The potentials  $(\phi, \mathbf{A})$  contain **four rather than six components** as in  $(\mathbf{E}, \mathbf{B})$ .
- ▶ They are obtained by solving the first, inhomogeneous pair of Maxwell's equations, which contains  $\rho$  and  $\mathbf{J}$ .

# Gauge transformations

- ▶ The scalar and vector potentials  $\phi$  and  $\mathbf{A}$  are **not unique**.
- ▶ Consider the following transformation of the potentials:

$$\left. \begin{aligned} \phi' &= \phi - \frac{\partial f}{\partial t} \\ \mathbf{A}' &= \mathbf{A} + \nabla f \end{aligned} \right\} f = f(q, t) \quad \leftarrow \text{gauge function of position and time}$$

- ▶ This **gauge transformation** of the potentials does not affect the physical fields:

$$\begin{aligned} \mathbf{E}' &= -\nabla\phi' - \frac{\partial\mathbf{A}'}{\partial t} = -\nabla\phi + \nabla\frac{\partial f}{\partial t} - \frac{\partial\mathbf{A}}{\partial t} - \frac{\partial\nabla f}{\partial t} = \mathbf{E} \\ \mathbf{B}' &= \nabla \times (\mathbf{A} + \nabla f) = \mathbf{B} + \nabla \times \nabla f = \mathbf{B} \end{aligned}$$

- ▶ We are free to choose  $f(q, t)$  so as to make  $\phi$  and  $\mathbf{A}$  satisfy additional conditions.
- ▶ In the **Coulomb gauge**, the gauge function is chosen such that the vector potential becomes **divergenceless**:

$$\nabla \cdot \mathbf{A} = 0 \quad \leftarrow \text{Coulomb gauge}$$

- ▶ Note: the Hamiltonian changes in the following manner upon a gauge transformation:

$$H' = H - z \frac{\partial f}{\partial t}$$

- ▶ However, the equations of motion are unaffected!

# The Hamiltonian in an electromagnetic field

- ▶ We must construct a Hamiltonian function such that  
Hamilton's equations are equivalent to Newton's equation with the Lorentz force:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \& \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \Leftrightarrow \quad m\mathbf{a} = z(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

- ▶ To this end, we introduce scalar and vector potentials  $\phi$  and  $\mathbf{A}$  such that

$$\mathbf{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}$$

- ▶ In terms of these potentials, the classical Hamiltonian function becomes

$$H = \frac{\pi^2}{2m} + z\phi, \quad \boldsymbol{\pi} = \mathbf{p} - z\mathbf{A} \quad \leftarrow \text{kinetic momentum}$$

- ▶ Quantization is then accomplished in the usual manner, by the substitutions

$$\mathbf{p} \rightarrow -i\hbar\nabla, \quad H \rightarrow i\hbar\frac{\partial}{\partial t}$$

- ▶ This gives the following time-dependent Schrödinger equation for a particle in an electromagnetic field:

$$i\hbar\frac{\partial\Psi}{\partial t} = \frac{1}{2m} (-i\hbar\nabla - z\mathbf{A}) \cdot (-i\hbar\nabla - z\mathbf{A})\Psi + z\phi\Psi$$



- ▶ According to our previous discussion, the **nonrelativistic Hamiltonian** for an electron in an electromagnetic field is given by:

$$H = \frac{\pi^2}{2m} - e\phi, \quad \pi = -i\hbar\nabla + e\mathbf{A}$$

- ▶ However, this description ignores a fundamental property of the electron: **spin**.
- ▶ Spin was **introduced by Pauli in 1927**, to fit experimental observations:

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m} \mathbf{B} \cdot \boldsymbol{\sigma} - e\phi$$

where  $\boldsymbol{\sigma}$  contains three operators, represented by the two-by-two Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- ▶ The Schrödinger equation now becomes a **two-component equation**:

$$\begin{pmatrix} \frac{\pi^2}{2m} - e\phi + \frac{e\hbar}{2m} B_z & \frac{e\hbar}{2m} (B_x - iB_y) \\ \frac{e\hbar}{2m} (B_x + iB_y) & \frac{\pi^2}{2m} - e\phi - \frac{e\hbar}{2m} B_z \end{pmatrix} \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix} = E \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix}$$

- ▶ the two components are only coupled **in the presence of an external magnetic field**

- ▶ The introduction of spin by Pauli in 1927 may appear somewhat ad hoc.
- ▶ By contrast, spin arises **naturally from Dirac's relativistic treatment** in 1928.
  - ▶ is spin a relativistic effect?
- ▶ However, **reduction of Dirac's equation to nonrelativistic form** yields the Hamiltonian

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m} \mathbf{B} \cdot \boldsymbol{\sigma} - e\phi \neq \frac{\pi^2}{2m} - e\phi$$

- ▶ in this sense, spin is not a relativistic property of the electron
  - ▶ but we note that, in the nonrelativistic limit, all magnetic fields disappear...
- ▶ Indeed, it is possible to take the **factorized form**

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi$$

as the starting point for a nonrelativistic treatment, with unspecified operators  $\boldsymbol{\sigma}$ .

- ▶ All algebraic properties of  $\boldsymbol{\sigma}$  then follow from the requirement  $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = p^2$ :

$$[\sigma_i, \sigma_j]_+ = 2\delta_{ij}, \quad [\sigma_i, \sigma_j]_- = 2\sum_k i\epsilon_{ijk}\sigma_k$$

- ▶ these operators are represented by the **two-by-two Pauli spin matrices**
- ▶ We interpret  $\boldsymbol{\sigma}$  by associating an **intrinsic angular momentum (spin)** with the electron:

$$\mathbf{s} = \hbar\boldsymbol{\sigma}/2$$

- ▶ The **nonrelativistic Hamiltonian** for an electron in an electromagnetic field is therefore

$$H = \frac{\pi^2}{2m} + \frac{e}{m} \mathbf{B} \cdot \mathbf{s} - e\phi, \quad \boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}, \quad \mathbf{p} = -i\hbar\nabla$$

- ▶ expanding  $\pi^2$  and assuming the **Coulomb gauge**  $\nabla \cdot \mathbf{A} = 0$ , we obtain

$$\begin{aligned} \pi^2\Psi &= (\mathbf{p} + e\mathbf{A}) \cdot (\mathbf{p} + e\mathbf{A})\Psi = p^2\Psi + e\mathbf{p} \cdot \mathbf{A}\Psi + e\mathbf{A} \cdot \mathbf{p}\Psi + e^2A^2\Psi \\ &= p^2\Psi + e(\mathbf{p} \cdot \mathbf{A})\Psi + 2e\mathbf{A} \cdot \mathbf{p}\Psi + e^2A^2\Psi = (p^2 + 2e\mathbf{A} \cdot \mathbf{p} + e^2A^2)\Psi \end{aligned}$$

- ▶ in **molecules**, the dominant electromagnetic contribution is from the **nuclear charges**:

$$\phi = -\frac{1}{4\pi\epsilon_0} \sum_K \frac{Z_K e}{r_K} + \phi_{\text{ext}}$$

- ▶ Summing over **all electrons** and adding **pairwise Coulomb interactions**, we obtain

$$\begin{aligned} H &= \sum_i \frac{1}{2m} p_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{K_i} \frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} r_{ij}^{-1} && \leftarrow \text{zero-order Hamiltonian} \\ &+ \frac{e}{m} \sum_i \mathbf{A}_i \cdot \mathbf{p}_i + \frac{e}{m} \sum_i \mathbf{B}_i \cdot \mathbf{s}_i - e \sum_i \phi_i && \leftarrow \text{first-order Hamiltonian} \\ &+ \frac{e^2}{2m} \sum_i A_i^2 && \leftarrow \text{second-order Hamiltonian} \end{aligned}$$

# Magnetic perturbations

- ▶ In atomic units, the **molecular Hamiltonian** is given by

$$H = H_0 + \underbrace{\sum_i \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i}_{\text{orbital paramagnetic}} + \underbrace{\sum_i \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{s}_i}_{\text{spin paramagnetic}} - \sum_i \phi(\mathbf{r}_i) + \underbrace{\frac{1}{2} \sum_i A^2(\mathbf{r}_i)}_{\text{diamagnetic}}$$

- ▶ There are two kinds of magnetic perturbation operators:
  - ▶ the **paramagnetic operator** is linear and may lower or raise the energy
  - ▶ the **diamagnetic operator** is quadratic and always raises the energy
- ▶ There are two kinds of paramagnetic operators:
  - ▶ the **orbital paramagnetic operator** couples the field to the electron's orbital motion
  - ▶ the **spin paramagnetic operator** couples the field to the electron's spin
- ▶ In the study of magnetic properties, we are interested in two types of perturbations:
  - ▶ **uniform external magnetic field**  $\mathbf{B}$ , with vector potential

$$\mathbf{A}_{\text{ext}}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r} \quad \text{leads to Zeeman interactions}$$

- ▶ **nuclear magnetic moments**  $\mathbf{M}_K$ , with vector potential

$$\mathbf{A}_{\text{nuc}}(\mathbf{r}) = \alpha^2 \sum_K \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3} \quad \text{leads to hyperfine interactions}$$

where  $\alpha \approx 1/137$  is the **fine-structure constant**

- ▶ We have studied the **nonrelativistic electronic Hamiltonian**:

$$H = H_0 + H^{(1)} + H^{(2)} = H_0 + \mathbf{A}(\mathbf{r}) \cdot \mathbf{p} + \mathbf{B}(\mathbf{r}) \cdot \mathbf{s} + \frac{1}{2}A(\mathbf{r})^2$$

where the **vector potential** in the Coulomb gauge is not unique but satisfies the relations

$$\nabla \times \mathbf{A}(\mathbf{r}) = \mathbf{B}(\mathbf{r}), \quad \nabla \cdot \mathbf{A}(\mathbf{r}) = 0$$

- ▶ We shall consider **uniform external field** and the **nuclear magnetic moments**:

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}_0, \quad \mathbf{A}_K(\mathbf{r}) = \alpha^2 \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3},$$

- ▶ First- and second-order **Rayleigh–Schrödinger perturbation theory** gives:

$$E^{(1)} = \langle 0 | \mathbf{A} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{s} | 0 \rangle$$

$$E^{(2)} = \frac{1}{2} \langle 0 | A^2 | 0 \rangle - \sum_n \frac{\langle 0 | \mathbf{A} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{s} | n \rangle \langle n | \mathbf{A} \cdot \mathbf{p} + \mathbf{B} \cdot \mathbf{s} | 0 \rangle}{E_n - E_0}$$

- ▶ We shall first consider external magnetic fields and next nuclear magnetic fields